Electrode Surface Fouling for Sensitive Electroanalytical Determination of Phenols

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Abstract
The present investigation of phenol and chlorophenols is conducted on the surface of glassy carbon by cyclic and square wave stripping voltammetry, and by Fourier-transform infrared spectroscopy. The surface fouling is accompanied by the appearance of reversible peaks at lower potential range (+0.1 to +0.4 V), that grew up with CV-cycling and attributed to the electro-redox reactions of formed polymer film via electropolymerization. The surface fouling is accompanied by the appearance of reversible peaks at lower potential range (+0.1 - +0.4 V vs. Ag/AgCl), that grew up with CV-cycling and attributed to the electro-redox reactions of formed polymer film via electropolymerization. The FT-IR supported by AM1 semi-empirical prediction attributes the electropolymerization to the formation of ortho-ortho and/or ortho-para C-C coupled systems. After proper optimizations of SWASV, the electroanalytical monitoring of one of the reversible-polymer oxidation peaks improved the detection limit of 2-chlorophenol (2CP) by 20 times of that obtained via monitoring its irreversible conventional peak. These detection limits of 2CP were 1.11 µM (140 ppb) and 18.99 µM (2.44 ppm) with reproducibility, for seven repeated measurements of 1.31% and 1.84%, respectively.

Cyclic voltammetry (CV) and square wave adsorptive stripping voltammetry (SWASV) are both potential controlled voltammetric techniques [1]. Therefore, it is possible to control the rate of oxidation and reduction (redox) reactions of phenols by varying the accumulation potential. To the best of our knowledge, the primary oxidation peak in Figure 1A (P1) obtained at a mild accumulation potential (+0.40 V) was the only one used in the electrochemical investigation and analytical determination of the 2CP using an acetylene black film modified glassy carbon electrode [2]. Other peaks along with P1 obtained by using accumulation potentials between +0.50 and +1.00 V, such as peak 2 (P2) and peak 3 (P3) of the phenol polymer were never considered for any analytical investigation of phenols, and their fouling influences were considered as obstacles toward sensing of the phenolic compounds.

In Figure 1A, the accumulation potential effect on the oxidation peak of 2-chlorophenol (2CP) using SWASV is presented. The result shows that accumulation potential of phenols helps on obtaining three peaks at a single scan. As the accumulation potential increases, the current magnitude of the first anodic oxidized peak (P1, \( E_{p1} \approx +0.60 \) V) decreases while the peaks of 2CP-polymer film (P2, \( E_{p2} \approx +0.30 \) V and P3, \( E_{p3} \approx +0.10 \)) drastically increases. Systematic investigation of the accumulation potential effect shown in Figure 1B indicates that P1 is the only obtained peak increases up to +400 mV, starts to be reduced and then levels off around +700 mV. From +500 mV, the observed reduction in P1 is accompanied by the appearance of the redox-active polymeric film’s peaks, P2 and P3, that increase subsequently with the increase of the accumulation potential applied value. At approximately +800 mV accumulation potential, the sensitivity of P1 signal is overtaken by P2 signal. The obtained results proved that P2 is promising and even competing with the conventional P1 for possible analytical determination of CPs.

References